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# (54) LITHOGRAPHIC PRINTING PLATE SUBSTRATE

#### (57) Abstract:

PROBLEM TO BE SOLVED: To manufacture a lithographic printing plate substrate having superior surface roughening efficiency in the electrochemical surface roughening, uniform pits and superior fitness and adherence to a printer as a lithographic printing plate.

SOLUTION: The surface roughening treatment including the electrochemical roughening is applied on the surface

of a plate material containing Fe: 0.05-0.5 wt.%, Si: 0.03-0.15 wt.%, Cu: 0.006-0.03 wt.% and Ti: 0.010-0.040 wt.% and also 1-100 ppm element or elements of at least one kind selected out of Li, Na, K, Rb, Cs, Ca, Sr, Ba, Sc, Y, Nb, Ta, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, C, Ge, P, As, S, Se, Te and Po and also containing unavoidable impurities and Al forming the remaining portion of the plate material, and the Al purity thereof is 99.0 wt.% or more.

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#### **CLAIMS**

[Claim(s)]

[Claim 1] Fe: 0.05 – 0.5wt% and Si:0.03 – 0.15wt%, Cu: 0.006 – 0.03wt% and Ti:0.010 – 0.040wt%, And at least one sort of elements chosen from Li, Na, K, Rb, Cs, calcium, Sr, Ba, Sc, Y, Nb, Ta, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, C, germanium, P, As, S, Se, Te, and Po The base material for the lithography versions characterized by coming to give split–face–ized processing which 1–100 ppm is contained, and the remainder consists of an unescapable impurity and aluminum, and includes electrochemical split–face–ization for the front face of a plate whose aluminum purity is more than 99.0wt%.

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### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention is excellent in the split-face-ized effectiveness at the time of electrochemical-split-face-ization-processing about the base material for the lithography versions, and relates to the base material for the lithography versions with a very uniform split-face-ized configuration.

[0002]

[Description of the Prior Art] Conventionally, the aluminum alloy plate is used as a base material for the lithography versions. And split-face-ized processing is performed in order that this aluminum alloy plate may give adhesion with a sensitization layer, and the water retention of the non-image section. It is the electrochemical split-face-ized method and acid solution which carry out electrolytic etching of the front face of an aluminium alloy plate from the former as the split-face-ized approach using the electrolytic solution which makes a subject mechanical split-face-ized methods, such as a ball grain and a brush grain, a hydrochloric acid, a nitric acid, etc. Although the chemical split-face-ized method which etches the front face of an aluminium alloy plate is learned, in recent years, the split face acquired by the electrochemical split-face-ized method has a homogeneous pit (irregularity), and since it excels in the printing engine performance, it is becoming in use to split-face-ize combining this electrochemical split-face-ized method and other split-face-ized approaches.

[0003] In connection with it, the attempt which gathers the effectiveness of electrolytic etching and reduces split-face-ized processing cost is made on the occasion of electrochemical splitface-ized processing, and examination about the alloy presentation of an aluminum alloy plate is also performed. For example, in JP,9-316582,A, it is about Fe:0.2 - 0.6wt% and Si:0.03 - 0.1wt% and Zn:0.04 - 0.10wt%. The aluminum alloy plate an implication and whose ratio of concentration (Zn/Fe) are 0.2 or more again to JP,9-279272,A Ti:0.005 - 0.05wt% and nickel:0.005 - 0.20wt% is included Si:0.03 - 0.15wt% Fe:0.2 - 0.6wt%. The aluminum alloy plate with which the intermetallic compound of these metals and aluminum serves as the amount of specification again and to JP,9-272937,A Ti:0.005 - 0.05wt% and nickel:0.005 - 0.20wt% is included Si:0.03 - 0.15wt% Fe:0.2 - 0.6wt%. furthermore, Cu, Zn:0.005 - 0.05wt%, In and Sn, and Pb:0.001 - 0.020wt% -- the included aluminum alloy plate -- moreover, to JP,9-289274,A Fe: 0.2 - 0.6wt% and Si:0.03 -0.15wt% and Ti:0.005 - 0.05wt% and nickel:0.005 - 0.20wt%, Ga: The aluminum alloy plate 0.005 -0.05wt%, a V:0.005-0.020wt% implication, and whose ratio of concentration (Ti+Ga)/V are 15 or less is indicated. The aluminum alloy plate indicated by these official reports means forming a uniform pit in spite of short-time electrolytic etching by adding the specific metal (Zn, nickel, In, Sn, Pb, Ti, V, Ga) which has the operation which adjusts the potential difference between an aluminum matrix and an intermetallic compound. [0004]

[Problem(s) to be Solved by the Invention] However, the wearing nature and adhesion of a printing machine to a printing cylinder when aluminum purity falling too much depending on balance with other components, and using as the lithography version the conventional aluminum alloy plate which was mentioned above while the initial complement of the specific metal added

caused many (they are dozens – thousands of range by ppm conversion) cost high worsen. [0005] It aims at offering the cheap base material for the lithography versions which this invention was made in view of such a situation, and was excellent in the split–face–ized effectiveness in electrochemical split–face–ized processing, and was excellent also in the wearing nature and adhesion to a printing machine when a pit being uniform and considering as the lithography version further.

[Means for Solving the Problem] the result of having repeated research wholeheartedly this invention persons solving the above-mentioned technical problem — a specific metal — the addition — \*\*\*\* — even if small, it finds out promoting the electrolytic etching of an aluminium alloy plate in electrochemical split-face-ized processing, and it came to complete this invention. The above-mentioned object Namely, this invention [Fe:0.05 — 0.5wt% of], and Si:0.03 — 0.15wt%, Cu: 0.006 — 0.03wt% and Ti:0.010 — 0.040wt%, And at least one sort of elements chosen from Li, Na, K, Rb, Cs, calcium, Sr, Ba, Sc, Y, Nb, Ta, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, C, germanium, P, As, S, Se, Te, and Po It is attained by the base material for the lithography versions characterized by coming to give split-face-ized processing which 1–100 ppm is contained, and the remainder consists of an unescapable impurity and aluminum, and includes electrochemical split-face-ization for the front face of a plate whose aluminum purity is more than 99.0wt%.

[0007]

[0006]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As for Fe, 0.05 -0.5wt% is added in the base material for the lithography versions of this invention. Fe is an element which combines with other elements in an aluminum alloy, and forms the eutectic compound of an aluminum-Fe system. Since the eutectic compound of this aluminum-Fe system has the effectiveness which forms a uniform electrolysis split face while making a recrystallization grain detailed, less than [ 0.05wt% ], this effectiveness is not acquired for the content of Fe, but the homogeneity of a pit falls with the lack of electrolysis. On the other hand, if Fe content exceeds 0.5wt(s)%, a big and rough compound will be formed and an electrolysis split-face-ized side will become an ununiformity. Moreover, when thinking the reinforcement when considering as a base material as important, it is desirable to make the content of Fe into 0.2 - 0.4wt%. Fe has the effectiveness which raises the mechanical strength of an aluminum alloy other than the above-mentioned effectiveness, therefore it lifting-comes to be easy of a version piece, in case a mechanical strength passes low and a content attaches in the printing cylinder of a printing machine as a lithography version less than [ 0.2wt% ]. On the other hand, since fitness nature comes to be inferior and it lifting-comes to be easy of a version piece during printing in case it will become the high intensity beyond the need and will attach in the printing cylinder of a printing machine as a lithography version, if a content exceeds 0.4wt(s)%, it is not desirable. The case of the printing version used for a proof application becomes however, less important for the constraint about these fitness nature or reinforcement.

[0008] Since Si is contained as an unescapable impurity in aluminum metal which is a raw material, in order that it may prevent the variation by the raw-material difference, minute amount addition of it is carried out intentionally in many cases. When the content exceeded 0.15wt(s)% and it prints at that time, there is nonconformity that the non-image section dirt-comes to be easy. On the other hand, since it may already have a content beyond 0.03wt% depending on a raw material, the numeric value below this is not realistic. Moreover, Si has the effectiveness which forms aluminum-Fe-Si system metallic compounds, and equalizes an electrolysis split face, therefore, less than [ 0.03wt% ], this effectiveness is not acquired for a content. Furthermore, since a high grade aluminum metal expensive in order to maintain less than [ 0.03wt% ] as a content is needed, it is not realistic from this point, therefore, the content of Si -- 0.03 - 0.15wt% -- it may be 0.04 - 0.10wt% preferably.

[0009] Cu is an element very important when controlling electrochemical split-face-ization. Therefore, since, a uniform pit is not formed. [resisting / of the scaling coat at the time of forming a pit electrochemically / a content ] [too little / less than / 0.006wt%] On the other hand, if a content exceeds 0.03wt(s)%, since resistance of the scaling coat at the time of forming

a pit in reverse will become excessive, a big and rough pit becomes is easy to be generated. The uniformity of this pit generation is an indispensable item in order to acquire the outstanding printability. therefore, the content of Cu -- 0.006 - 0.03wt% -- it may be 0.01 - 0.02wt% preferably.

[0010] Ti is added in order to make detailed conventionally the crystalline structure at the time of casting. this invention — 0.010 – 0.040wt% — it is the form of an aluminum—Ti alloy 0.020 – 0.030wt% of preferably, or is added in the form of an aluminum—B—Ti alloy. Since resistance of the scaling coat at the time of forming a pit in electrochemical split—face—ized processing becomes [ too little ] when an addition exceeds 0.040wt(s)%, the nonconformity that a uniform pit is no longer formed arises. There is nonconformity of on the other hand producing a defect with the trace of the cast structure where it is big and rough even after an addition makes the thickness of 0.1–0.5mm through various processes, since cast structure is not made detailed less than [ 0.010wt% ] remarkable in \*\*\*\*\*\* and an appearance.

[0011] In this invention, it is characterized by carrying out minute amount addition of at least one sort of elements chosen from Li, Na, K, Rb, Cs, calcium, Sr, Ba, Sc, Y, Nb, Ta, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, C, germanium, P, As, S, Se, Te, and Po in addition to the above-mentioned component. In electrochemical split-face-ized processing, these elements promote electrolytic etching, have the effectiveness of raising the homogeneity of a pit, and, moreover, discover the effectiveness in \*\*\*\* small quantity. As an addition, if at least 1 ppm adds, it is enough. Moreover, the addition beyond the need is 100 ppm or less as an upper limit desirably from a viewpoint of profitability. Therefore, physical properties demanded as a base material for the lithography versions, such as a mechanical strength and flexibility, are not affected at all. In addition, two or more sorts of above-mentioned additions are those sum totals, when using together. Moreover, in case it casts after fusing aluminum metal and preparing to a predetermined alloy content as the addition approach of these elements, the approach of adding as a raw material, the approach of adding in the processing liquid in electrochemical split-face-ized down stream processing, or the approach of adding at an upstream process from electrochemical split-face-ized down stream processing can be adopted.

[0012] Although it is an unescapable impurity and aluminum except each component mentioned above, in this invention, the aluminum purity of an aluminum alloy needs to be more than 99.0wt%. If the mechanical strength of an aluminum alloy usually has low aluminum purity depending on aluminum purity, the flexibility of an aluminum alloy will become low. Therefore, if the content of the component mentioned above becomes high too much, nonconformity, like the wearing nature to the printing machine when considering as the base material for the lithography versions worsens will come to arise.

[0013] The following approach is employable in order to make the above-mentioned aluminum alloy into a plate. First, according to a conventional method, defecation processing is performed and the aluminum alloy molten metal adjusted to the predetermined alloy content is cast. The filter which uses the so-called rigid media filters, such as degasifying processing using flux processing, Ar gas, Cl gas, etc., and a ceramic-tube filter, a ceramic form filter, an alumina flake, alumina balls, etc. as a filtering medium in order to remove unnecessary gas, such as hydrogen in a molten metal, in defecation processing, and filtering using a grass cloth filter etc. Or processing which combined degasifying and filtering is performed.

[0014] Subsequently, the above-mentioned molten metal is cast. About the casting approach, there are an approach using fixed mold represented by the direct chill casting process and an approach using actuation mold represented by the continuous casting process, and any approach is possible. For example, when DC casting is performed, the ingot of 300-800mm of board thickness can be manufactured. the ingot — a conventional method — following — facing — a surface — 1–10mm is cut desirably 1–30mm. Then, soak-ized processing is performed if needed. When performing soak-ized processing, heat treatment of 1 hours or more and 48 hours or less is performed at 450-620 degrees C so that an intermetallic compound may not make it big and rough. When shorter than 1 hour, the effectiveness of soak-ized processing serves as imperfection. Subsequently, hot rolling and cold rolling are performed and it considers as an aluminum rolled plate. As initiation temperature of hot rolling, it considers as the range of 350—

500 degrees C. Intermediate-annealing processing may be performed to the middle a front or the back. [ cold rolling ] The heat-treatment for 120 or less seconds can be desirably used for the intermediate-annealing conditions in this case at 450-550 degrees C 360 or less seconds by 400-600 degrees C using the approach of heating at 350-500 degrees C desirably by 280 degrees C - 600 degrees C for 2 to 10 hours for 2 to 20 hours using a batch type annealing furnace, and a continuous annealing furnace. The crystalline structure can also be made fine if it heats with the programming rate of 10 degrees C/second or more using a continuous annealing furnace. Predetermined thickness, for example, the aluminium alloy plate to which 0.1-0.5mm was made, may improve smoothness by orthodontic appliance, such as a roller leveler and a tension leveler, further like the above. Moreover, in order to process a board width into predetermined width, letting a slitting machine line pass is also usually performed.

[0015] Thus, split-face-ized processing is performed in order to use the made aluminum alloy plate as the base material for the lithography versions subsequently. As mentioned above, it is desirable for the aluminum alloy plate of this invention to fit electrochemical split-face-ized processing, therefore to combine suitably electrochemical split-face-ized processing, and mechanical split-face-ized processing and/or chemical split-face-ized processing as split-faceized processing. Since electrochemical split-face-ized processing is easy to give detailed irregularity to the front face of an aluminum alloy plate, it is suitable for making the lithography version which was excellent in printing nature. This electrochemical split-face-ized processing is performed in the water solution which makes a nitric acid or a hydrochloric acid a subject using a direct current or an alternating current. The pit of the shape of a crater with an average diameter of about 0.5-20 micrometers or a honeycomb is generable at 30 - 100% of rate of area on an aluminum front face with this split-face-ization. The pit prepared here has the operation which improves the dirt hard and print durability of the non-image section of the printing version. Moreover, in electrochemical split-face-ized processing, a product with quantity of electricity which is required in order to establish sufficient pit in a front face, i.e., a current, and the resistance welding time serves as important conditions in the formation of an electrochemical split face. It is desirable also from a viewpoint of energy saving that pit sufficient with smaller quantity of electricity can be formed. In this invention, although especially the terms and conditions of this electrochemical split-face-ized processing are not limited and can be performed on general conditions, in any case, necessary quantity of electricity is substantially reducible.

[0016] Mechanical split-face-ized processing combined with this is performed in order to make an aluminum alloy plate front face into 0.35–1.0 micrometers of average surface roughness generally. In this invention, especially the terms and conditions of this mechanical split-face-ized processing can be performed according to the approach indicated by JP,6–135175,A and JP,50–40047,B, for example, although not restricted. Moreover, especially chemical split-face-ized processing is not restricted, either and a well-known approach can be followed.

[0017] Although anodizing is performed in order to continue at the above-mentioned split-face-ized processing and to usually raise the abrasion resistance of the front face of an aluminum alloy plate, it is desirable to perform anodizing also in this invention. Anythings can be used if a porosity oxide film is formed as an electrolyte used for this anodizing. Generally a sulfuric acid, a phosphoric acid, oxalic acid, chromic acids, or those mixed liquor are used. The concentration of those electrolytes is suitably decided according to an electrolytic class. Since the processing conditions of anodic oxidation change with the electrolyte to be used, it cannot generally specify, but generally, 1 – 80wt%, electrolytic concentration is suitable for it, if solution temperature is in 5–70 degrees C, current density 1 – 60 A/dm2, electrical potential differences 1–100V, and the range for 10 seconds – electrolysis time amount 300 seconds.

[0018] Moreover, in order to improve the dirt engine performance at the time of printing, it may rinse, after it rinses after performing electrochemical split-face-ized processing and rinsing and an alkali solution performs slight etching processing, and H2SO4 solution performs De Dis Matt, and direct-current electrolysis may be succeedingly performed in H2SO4 solution, and an anodic oxide film may be prepared. Furthermore, hydrophilization processing by silicate etc. may be performed if needed.

[0019] Although the base material for the lithography versions of this invention is obtained as mentioned above, this base material has the high homogeneity of a pit, and the lithography version excellent in the printing engine performance is obtained. What is necessary is to apply and dry sensitization material and just to form a sensitization layer in a front face, in order to consider as the lithography version. In addition, especially sensitization material is not limited and can usually use what is used for the photosensitive lithography version. And it can consider as the printing version which can attach an image in a printing machine by performing baking and a development, and gum length processing using a lith film. Moreover, if a high sensitivity sensitization layer is prepared, an image can also be directly burned using laser. [0020]

[Example] The aluminum alloy of the presentation shown in a table 1 was spent on \*\*-SU, as shown in a table 2 at this, various elements were added and the aluminum alloy plate of an example and the example of a comparison was created. And the following split-face-ized processings were performed about each aluminum alloy plate. First, the NaOH solution performed etching processing, after [rinsing] HNO3 solution performed the desmut treatment, and electrochemical split-face-ized processing was further performed by performing alternating current electrolysis in after [ rinsing ] HNO3 solution. After rinsing, in order to remove the smut produced in electrochemical split-face-ized processing, H2SO4 solution performed De Dis Matt. [0021] Quantity of electricity taken to make a uniform pit on the whole surface was investigated and evaluated about each example and the example of a comparison here. Moreover, the homogeneity of the pit at that time was also doubled and evaluated. In order to investigate quantity of electricity by which a pit is made on the whole surface, after changing the quantity of electricity conditions and performing electrochemical split-face-ized processing, the front face was observed using SEM and quantity of electricity which the pit has formed in the whole surface was determined. The homogeneity of a pit carried out SEM observation and judged the split face. The result was shown in a table 2. In addition, quantity of electricity is the relative value which set the example -1 of a comparison to 1. [0022]

[A table 1]

	表1							
成分	Si	Fe	Cu	Mn	Mg	Zn	Ti	
0	0.06	0.30	0.017	0.001	0.001	0.001	0.03	
2	0.15	0.35	0.006	0.001	0.010	0.001	0.03	

[0023] [A table 2]

			表 2		
				ピット全面形成に必要	
		添加	添加量	な微気量	とっトの
. (	基本成分	元素	(ppm)	比較例-1を1として比	均一性
				較	
実施例-1	成分①	Li	10	0.9	
実施例-2	成分①	Na	10	0.9	
実施例-3	成分①	K	10		
実施例-4	成分①	Rь	10		
実施例一5	成分①	Cs	10		
実施例一6	成分①	Ca	10	0.9	
実施例-7	成分①	Sr	10		
実施例-8	成分①	Ва	10		
実施例-9	成分①	Sc	10		
実施例-10	成分①	Υ	10		
実施例-11	成分①	Nb	10		
実施例-12	成分①	Υa	10		
実施例-13	成分①	Мо	10		
実施例-14	成分①	W	10		
実施例-15	成分①	Tc	10		
実施例-16	成分①	Re	10		
実施例-17	成分①	Rυ	10	The second secon	
実施例-18	成分①	Os	10	<del></del>	
実施例-19	成分①	Rh	10		
実施例ー20	成分①	lr_	10		
実施例-21	成分①	Pd	10		
実施例-22	成分①	Pt	10		
実施例-23	成分①	Ag	10		良
実施例-24	成分①	Au	10		良
実施例-25	成分①	<u> c</u>	10		良
実施例-26	成分①	Ge	10		良
実施例一27	成分①	Р	10		
実施例-28	成分①	As	10		
実施例-29	成分①	S	10		良
実施例-30		Se	10		良
実施例-31	成分①	Te	10		良
実施例-32	成分①	Po	10		良
実施例-33		Мо	100	<del></del>	<del> </del>
実施例一34		Мо	10	<u> </u>	良
比較例-1	成分①	無し	1		回
比較例一2	成分②	無し	-	1	i] <u> </u>

[0024] The aluminum alloy plate of an example is having added the specific element, and can be used as the base material for the lithography versions in which the effectiveness of electrochemical split-face-ized processing improved about ten percent, and the homogeneity of a pit was further excellent as shown in a table 2.

[0025] Although the above example showed the example which performed only electrochemical split-face-ized processing as split-face-ized processing, even if this invention is not limited to the above-mentioned example, for example, it combines mechanical split-face-ized processing and chemical split-face-ized processing with electrochemical split-face-ized processing, it cannot be overemphasized that the same effectiveness is acquired.

[0026]

[Effect of the Invention] As explained above, according to this invention, the base material for the lithography versions the effectiveness of electrochemical split-face-ized processing improved about ten percent, and the homogeneity of a pit excelled [ base material ] in having added the specific element further is obtained.

[Translation done.]